17.5 SOLUTIONS OF STRONG ELECTROLYTES

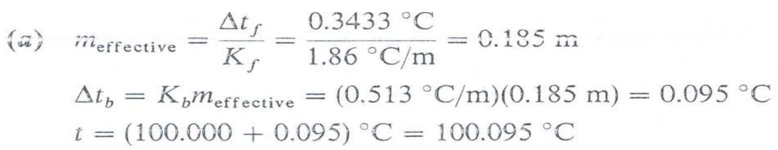
17.85 Of the following 0.10 m aqueous solution, which one will exhibit the largest freezing point depression? (a) KCl (b) $C_6H_{12}O_6$ (c) K_2SO_4 (d) $Al_2(SO_4)_3$ (e) NaCl

- KCl has 2 ions per formula unit. $C_6H_{12}O_6$ has 1 molecular per formula unit. K_2SO_4 has 3 ions per formula unit. $Al_2(SO_4)_3$ has 5 ions per formula unit. NaCl has 2 ions per formula unit. $Al_2(SO_4)_3$ thus has the greatest freezing point depression.

17.86 Arrange the following aqueous solutions in order of increasing freezing points (that is, lowest first): (a) 0.10 m C_2H_5OH (b) 0.10 m $Ba_3(PO_4)_2$ (c) 0.10 m Na_2SO_4 (d) 0.10 KCl (e) 0.10 m Li_3PO_4

- b < e < c < d < a. $Ba_3(PO_4)_2$ has 5 mol of ions per mol of formula units; Li_3PO_4 has 4 ; Na_2SO_4 has 3; and KCl has 2 . C_2H_5OH is not ionic; it has 1 mol of molecules per mol of formula units.

17.87 A 0.100 m solution of $NaClO_3$ freezes at -0.3433 °C. What would you predict for the boiling point of this aqueous solution at 1 atm pressure? At 0.00100 m concentration of this same salt, the electrical interferences between the ions no longer exist, because the ions are, on the average, too far apart from each other. Predict the freezing point of this more dilute solution.



(a) $m_{\text{effective}} = \dfrac{\Delta t_f}{K_f} = \dfrac{0.3433\ °C}{1.86\ °C/m} = 0.185\ m$

$\Delta t_b = K_b m_{\text{effective}} = (0.513\ °C/m)(0.185\ m) = 0.095\ °C$

$t = (100.000 + 0.095)\ °C = 100.095\ °C$

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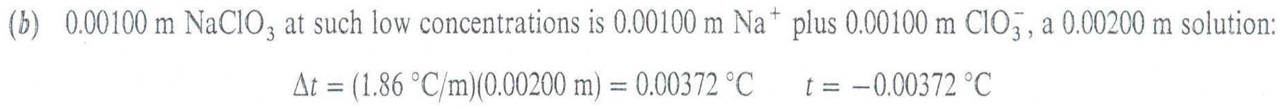

(b) 0.00100 m $NaClO_3$ at such low concentrations is 0.00100 m Na^+ plus 0.00100 m ClO_3^-, a 0.00200 m solution:

$\Delta t = (1.86\ °C/m)(0.00200\ m) = 0.00372\ °C \qquad t = -0.00372\ °C$

17.88 Estimate the equivalent conductivity at infinite dilution for $HClO_4$, using the data of Tables 17.3 and 17.4.

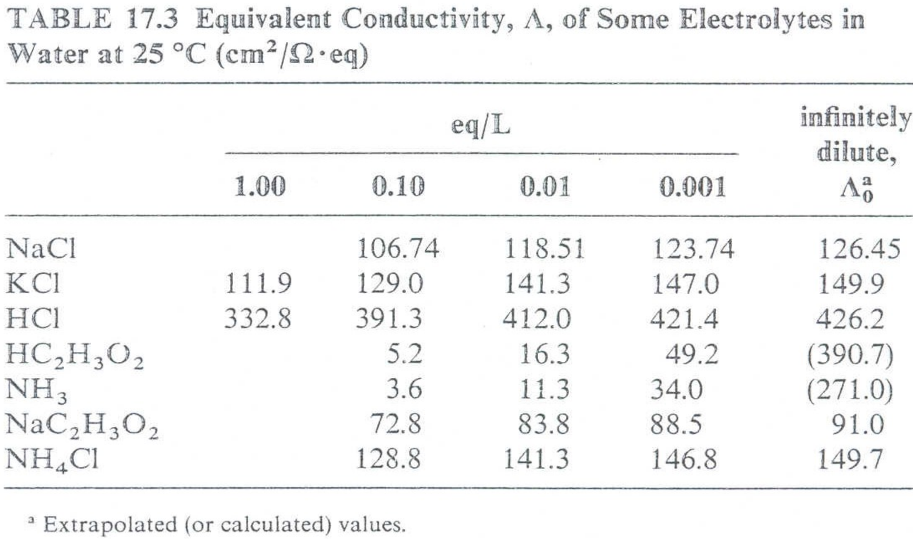

TABLE 17.3 Equivalent Conductivity, Λ, of Some Electrolytes in Water at 25 °C ($cm^2/\Omega \cdot eq$)

	eq/L				infinitely dilute, Λ_0^a
	1.00	0.10	0.01	0.001	
NaCl		106.74	118.51	123.74	126.45
KCl	111.9	129.0	141.3	147.0	149.9
HCl	332.8	391.3	412.0	421.4	426.2
$HC_2H_3O_2$		5.2	16.3	49.2	(390.7)
NH_3		3.6	11.3	34.0	(271.0)
$NaC_2H_3O_2$		72.8	83.8	88.5	91.0
NH_4Cl		128.8	141.3	146.8	149.7

[a] Extrapolated (or calculated) values.

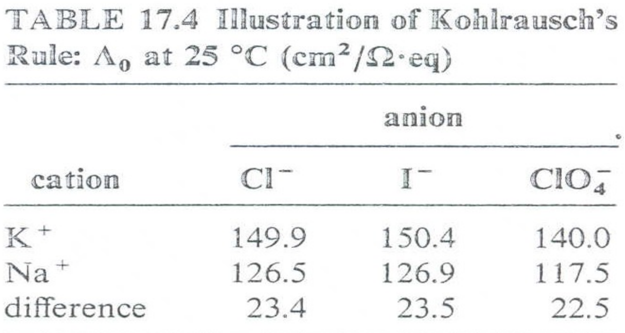

TABLE 17.4 Illustration of Kohlrausch's Rule: Λ_0 at 25 °C ($cm^2/\Omega \cdot eq$)

	anion		
cation	Cl^-	I^-	ClO_4^-
K^+	149.9	150.4	140.0
Na^+	126.5	126.9	117.5
difference	23.4	23.5	22.5

- $\Lambda_0(HClO_4) = \Lambda_0(HCl) + \Lambda_0(NaClO_4) - \Lambda_0(NaCl) = 426.2 + 117.5 - 126.5 = 417.2\ cm^2/\Omega \cdot eq$

17.89 Show how the equivalent conductivity at infinite dilution for acetic acid was calculated from other data in Table 17.3.

- $\Lambda_0(HC_2H_3O_2) = \Lambda_0(NaC_2H_3O_2) + \Lambda_0(HCl) - \Lambda_0(NaCl) = 91.0 + 426.2 - 126.5 = 390.7\ cm^2/\Omega \cdot eq$

17.90 The equivalent conductivity of a solution containing 2.54 g of $CuSO_4$/L is 91.$cm^2/\Omega \cdot eq.$ (a) Calculate the specific conductivity of the solution. (b) What is the resistance of cm^3 of this solution when placed between two electrodes 1.00 cm apart, each having an area of 1.00 cm^2?

- $$(a)\quad \Lambda = \frac{\kappa}{C}, \qquad \text{where } C = N/1000 = \text{eq/cm}^3$$
  $$\left(\frac{2.54\text{ g CuSO}_4}{\text{L}}\right)\left(\frac{1\text{ mol}}{159.5\text{ g}}\right)\left(\frac{2\text{ eq}}{\text{mol}}\right) = 0.0318\text{ N CuSO}_4$$
  $$\kappa = \left(\frac{91.0\text{ cm}^2}{\Omega\cdot\text{eq}}\right)\left(\frac{0.0318\text{ eq}}{1000\text{ cm}^3}\right) = 2.89\times10^{-3}\ \Omega^{-1}\cdot\text{cm}^{-1}$$
  $$(b)\quad R = \frac{1}{\kappa}\frac{l}{A} = \left(\frac{1}{2.89\times10^{-3}\ \Omega^{-1}\cdot\text{cm}^{-1}}\right)\left(\frac{1.00\text{ cm}}{1.00\text{ cm}^2}\right) = 346\ \Omega$$

17.91 The equivalent conductivity of a 0.0100 M aqueous solution of ammonia is 10 $cm^2/\Omega \cdot eq$. The equivalent conductivity of ammonia at infinite dilution is calculated to be 238 $cm^2/\Omega \cdot eq$. Calculate the percent ionization of ammonia in 0.0100 M aqueous solution.

$$\frac{10\text{ cm}^2/\Omega\cdot\text{eq}}{238\text{ cm}^2/\Omega\cdot\text{eq}}\times 100\% = 4.2\%\text{ ionized}$$

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17.92 The freezing point of solution composed of 10.0 g KCl in 100 g of water is -4.5 °C. Calculate the van’t Hoff factor, *i*, for this solution.

- $$\Delta t = iKm$$
  $$m = \frac{100\text{ g/kg H}_2\text{O}}{74.55\text{ g/mol}} = 1.34\text{ m}$$
  $$i = \frac{\Delta t}{Km} = \frac{4.5\ ^\circ\text{C}}{(1.86\ ^\circ\text{C/m})(1.34\text{ m})} = 1.8$$

17.93 For each of the following statements about the nature of aqueous solutions of strong electrolytes (a) give the experimental observations which tend to support the statement and (b) suggest experimental methods for proving or disproving the statement.

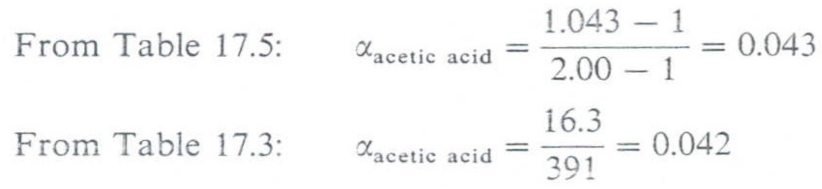
(i) Ions are formed when charged electrodes are placed in a solution of a strong electrolyte.

(ii) Ions are formed when strong electrolytes are dissolved in water.

(iii) Not only is it unnecessary to dissolve an electrolyte in water in order for ions to exist, but in solution there is considerable interionic attraction.

- (i) For strong electrolytes, the ions are present even before immersion of charged electrodes in the solution. Early experiments could not prove the presence of ions except by electrolysis. Freezing point depression methods prove that ions are present even in the absence of electrodes. (ii) Only for strong acids does the solution process produce ion. Most strong electrolytes, 100% ionized in solution, are ionic even in the pure state. The conductivity of molten salts proves that the existence of ions does not depend on the solution process for salts. The conductivity of molten salts proves that existence of ions does not depend on the solution process for salts. (The absence of conductivity in such strong acids as pure liquid HI shows that these compounds are covalent when pure and form ions by reaction with the solvents.) (iii) The conductivity of molten salts proves the first statement; the values of i lower than the number of ions per formula unit proves the second. Statement iii is the present theory of strong electrolytes.

17.94 Calculate the value of α for 0.010 m aqueous acetic acid from the data of Table 17.5 and again from the data of Table 17.3.



From Table 17.5: $\alpha_{\text{acetic acid}} = \frac{1.043 - 1}{2.00 - 1} = 0.043$

- From Table 17.3: $\alpha_{\text{acetic acid}} = \frac{16.3}{391} = 0.042$

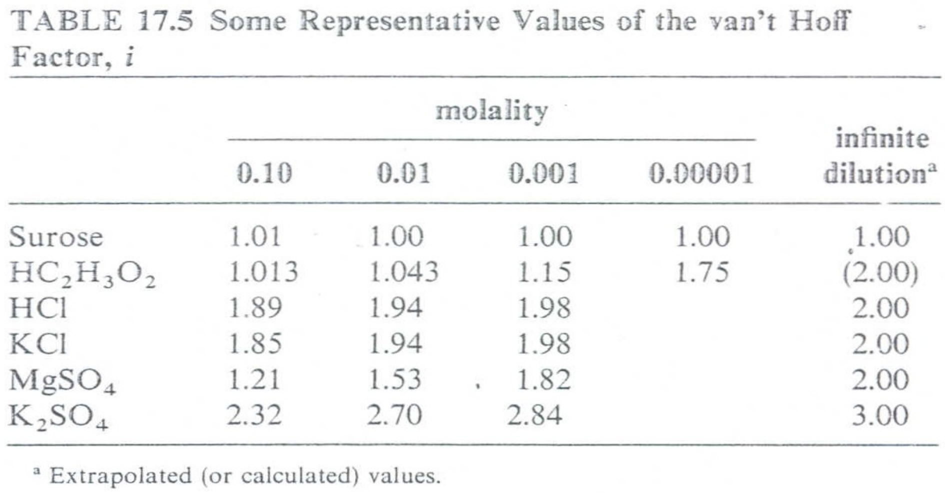


TABLE 17.5 Some Representative Values of the van't Hoff Factor, *i*

	molality				infinite dilution[a]
	0.10	0.01	0.001	0.00001	
Surose	1.01	1.00	1.00	1.00	1.00
$HC_2H_3O_2$	1.013	1.043	1.15	1.75	(2.00)
HCl	1.89	1.94	1.98		2.00
KCl	1.85	1.94	1.98		2.00
$MgSO_4$	1.21	1.53	1.82		2.00
K_2SO_4	2.32	2.70	2.84		3.00

[a] Extrapolated (or calculated) values.

17.95 Using the data of Table 17.5 calculate the value of K_a for a 0.010 M solution of acetic acid. As shown above, the value of α for acetic acid in 0.010 M solution is 0.043:

$$K_a = \frac{(0.043)^2(0.010)}{0.957} = 1.9 \times 10^{-5}$$

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17. 96 Estimate the equivalent conductivity of Na_2SO_4 in 0.00100 N solutions from the following equivalent conductivities in 0.00100 N solutions: NaCl, 123.7 cm^3/Ω$\cdot eq$; K_2SO_4, 152.1 cm^2/$\Omega \cdot eq$;

- $$\begin{aligned} &\Lambda(K_2SO_4) + \Lambda(NaCl) - \Lambda(KCl) = \Lambda(Na_2SO_4) \\ &\quad 152.1 \quad + \quad 123.7 \quad - \quad 147.0 \quad = 128.8\ \text{cm}^2/\Omega\cdot\text{eq} \end{aligned}$$

(Note that for equivalent conductivities, the value for K_2SO_4 and Na_2SO_4 are not halved.)

17.97 Estimate the equivalent conductivity of a 0.0100 M acetic acid solution from its conductivity at infinite dilution, 390.7 cm^2/Ω$\cdot eq$ at 25 °C, and the value of its dissociation constant, K_a = 1.8 x a0^{-5}.

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

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Let $x = [H_3O^+]$

then $x = [C_2H_3O_2^-]$ and $0.0100 - x = [HC_2H_3O_2]$

$$K_a = \frac{x^2}{0.0100 - x} = 1.8 \times 10^{-5} \simeq \frac{x^2}{0.0100}.$$

$$x^2 = 1.8 \times 10^{-7}$$

$$x = 4.2 \times 10^{-4}$$

$$\frac{\Lambda}{\Lambda_0} = \frac{4.2 \times 10^{-4}}{1.0 \times 10^{-2}} = \frac{\Lambda}{390.7} = 4.2 \times 10^{-2}$$

$$\Lambda = (390.7)(4.2 \times 10^{-2}) = 16\ \text{cm}^2/\Omega\cdot\text{eq}$$

17.98 Chloroacetic acid, a monoprotic has a K_a of 1.36 x 10^{-3}. Compute the freezing point of a 0.10 M solution of this acid. Assume that the stoichiometric molar concentration and molality are the same in this case.

- $HC_2H_2ClO_2 + H_2O \rightleftharpoons C_2H_2ClO_2^- + H_3O^+ \qquad K_a = \frac{[H_3O^+][C_2H_2ClO_2^-]}{[HC_2H_2ClO_2]} = 1.36 \times 10^{-3}$

$$\frac{x^2}{0.10 - x} = 1.36 \times 10^{-3}$$

$$x^2 = 1.36 \times 10^{-4} - (1.36 \times 10^{-3})x$$

$$x^2 + (1.36 \times 10^{-3})x - 1.36 \times 10^{-4} = 0$$

$$x = \frac{-1.36 \times 10^{-3} + \sqrt{(1.36 \times 10^{-3})^2 - 4(-1.36 \times 10^{-4})}}{2} = 0.0110\ M$$

$$[C_2H_2ClO_2^-] = [H_3O^+] = 1.10 \times 10^{-2} \qquad [HC_2H_2ClO_2] = 0.10 - 1.10 \times 10^{-2} = 0.09\ M$$

$$\text{Total solute particles} = [C_2H_2ClO_2H] + [C_2H_2ClO_2^-] + [H_3O^+] = 0.112\ M \approx 0.112\ m$$

$$\Delta t = K_f m = (-1.86\ ^\circ C/m)(0.112\ m) = -0.21\ ^\circ C$$

17.99 A 0.025 M solution of monobasic acid had a freezing point of -0.060 °C. What are K_a and pK_a for the acid ?

- $m = \frac{\Delta t}{K_b} = -(0.060°C)/(-1.86\ °C/m) = 3.2 \times 10^{-2} \approx 3.2 \times 10^{-2}$ M of total particles

Each molecule which ionizes increase the number of solute particles by one.

$HA \leftrightarrow H^+ + A^-$

The increase in the number of particles is therefore equal to the number of each of ion. As a result, there is (0.032-0.025) M = 0.007 M H^+, 0.007 M A^-, and 0.018 M HA in the solution:

$K_a = \frac{(0.007)^2}{0.018} = 3 \times 10^{-3} \qquad pK_a = 2.5$

17.100 A 0.100 M solution of an acid (density = 1.010 g/cm^3) is 4.5% ionized. Compute the freezing point of the solution. The molecular weight of the acid is 300.

- We must first determine the molality of the solutions, i.e., the number of moles of acid dissolved in 1 kg of water.
  Mass of 1.00 0L of solution = (1000cm^3)(1.010 g/cm^3) = 1010 g
  Mass of solute in 1.000 L solution = (0.100 mol) (300 g/mol) = 30 g
  Mass of water in 1.000 L of solution = (1010-30)g =980 g
  Molality of solution = 0.100 mol acid/0.980 kg water = 0.102 mol/kg

  If the acid were not ionized at all, the freezing point lower would be 1.86x0.102=0.190$^{\circ}C$

Because of ionization, the total number of dissolved particles is greater than 0.102 mol/kg of solvent, the freezing point depression is determined by the total number of dissolved particles, regardless of whether they are charged or uncharged.

Let α = fraction ionized. For every mol of acid added to the solution, there will be (1-α) mol of un-ionized acid at equilibrium, $\alpha\ mol\ of\ H^{+}$, and $\alpha\ mol\ of\ anion\ base\ conjugate$ to the acid, or a total of (1+α)mol of dissolved particles. Hence the molality with respect to all dissolved particles is (1+α) times the molality computed without regard to ionization.

Freezing point depression = (1+α)(0.190$^{\circ}C$)= (1.045)(0.190$^{\circ}C$) = 0.199$^{\circ}C$

The freezing point of the solution is -0.199$^{\circ}C$

17.101 Explain why 0.100 m NaCl in water does not have a freezing point equal to (a) -0.183$^{\circ}C$ (b) -0.366$^{\circ}C$

- (a) There are 2 mol of ions per mol of NaCl. (b) There is interionic attraction, which reduces somewhat the independence of the ions and therefore their effect on the freezing point. (The value of i is somewhat below 2.)

17.102 State one method by which one could distinguish between the compounds $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

- The compound can be distinguished by their conductivities [as well as by their infrared spectra (coordinated sulfate is not tetrahedral in its vibrational motions), x-ray diffraction, and chemical methods].